

(19) World Intellectual Property Organization  
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**WO 02/02691 A1**

(51) International Patent Classification<sup>7</sup>: **C08L 51/04,**  
53/02

(21) International Application Number: **PCT/KR00/01258**

(22) International Filing Date:  
3 November 2000 (03.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2000/38651 6 July 2000 (06.07.2000) KR

(71) Applicant (for all designated States except US): **LG  
CHEMICAL CO., LTD.** [KR/KR]; LG Twin Tower,  
Yoido-dong 20, Yongdungpo-ku, Seoul 150-721 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **YOO, Keun-Hoon**

[KR/KR]; Hanvit Apt. 123-801, Ahun-dong, Yusung-ku,  
Taejeon-city 305-333 (KR). **CHOI, Jeong-Su** [KR/KR];  
LG Ansan Sataek Sinkwan 307, Ansan-dong, Yosu-city,  
Chollanam-do 555-050 (KR). **KIM, Sung-Hee** [KR/KR];  
LG Ansan Sataek 2 dong 405, Ansan-dong, Yosu-city,  
Chollanam-do 503-232 (KR). **LEE, Chan-Hong**  
[KR/KR]; Lucky Hana Apt. 102-901, Sinsung-dong,  
Yusung-ku, Taejeon-city 305-345 (KR).

(74) Agent: **KIM, Won-Ho**; 7th Fl., Teheran Bldg., 825-33,  
Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).

(81) Designated States (national): CN, DE, JP, US.

(84) Designated State (regional): European patent (FR).

Published:  
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/02691 A1

(54) Title: **PROCESS FOR PREPARING THERMOPLASTIC TRANSPARENT RESIN**

(57) Abstract: The present invention relates to a process for preparing thermoplastic transparent resin, and provides a process for preparing thermoplastic transparent resin comprising the steps of: (¥) preparing graft transparent resin by grafting a monomer mixture comprising 20 to 50 parts by weight of conjugated diene rubber latex, 10 to 50 parts by weight of methacrylic acid alkylester compound or acrylic acid alkylester compound, 5 to 25 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of vinylcyan compound through emulsion polymerization; (¥¢) preparing methylmethacrylate-styrene-acrylonitrile (hereinafter referred to as "MSAN") copolymer by copolymerizing 50 to 75 parts by weight of methacrylic acid alkylester compound or alkylester compound, 20 to 45 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of vinylcyan compound during bulk polymerization; and (¥) blending the graft transparent resin of step ¥) with the MSAN copolymer of step ¥¢). The thermoplastic transparent resin prepared by the present invention is good in terms of impact resistance, chemical resistance, processibility, etc., has superior moisture and heat resistance, natural color, etc., and extremely superior transparency.

## PCT REQUEST

OPP000659KR

Original (for SUBMISSION) - printed on 03.11.2000 09:27:12 AM

0 0-1	For receiving Office use only International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4 0-4-1	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.91 (updated 10.10.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Korean Industrial Property Office (RO/KR)
0-7	Applicant's or agent's file reference	OPP000659KR
I	Title of invention	PROCESS FOR PREPARING THERMOPLASTIC TRANSPARENT RESIN
II II-1 II-2 II-4 II-5	Applicant This person is: Applicant for Name Address:	applicant only all designated States except US LG CHEMICAL LTD. LG Twin Tower Yoido-dong 20, Yongdungpo-ku, 150-721 Seoul Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	82-42-866-2072
II-9	Facsimile No.	82-42-861-4152
III-1 III-1-1 III-1-2 III-1-4 III-1-5	Applicant and/or inventor This person is: Applicant for Name (LAST, First) Address:	applicant and inventor US only YOO, Keun-Hoon Hanvit Apt. 123-801 Ahun-dong, Yusung-ku 305-333 Taejeon-city Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

## PCT REQUEST

OPP000659KR

Original (for SUBMISSION) - printed on 03.11.2000 09:27:12 AM

III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	CHOI, Jeong-Su
III-2-5	Address:	LG Ansan Sataek Sinkwan 307 Ansan-dong 555-050 Yosu-city, Chollanam-do Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	KIM, Sung-Hee
III-3-5	Address:	LG Ansan Sataek 2 dong 405 Ansan-dong 503-232 Yosu-city, Chollanam-do Republic of Korea
III-3-6	State of nationality	KR
III-3-7	State of residence	KR
III-4	Applicant and/or inventor	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	LEE, Chan-Hong
III-4-5	Address:	Lucky Hana Apt. 102-901 Sinsung-dong, Yusung-ku 305-345 Taejeon-city Republic of Korea
III-4-6	State of nationality	KR
III-4-7	State of residence	KR
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	KIM, Won-Ho
IV-1-2	Address:	7th Fl., Teheran Bldg., 825-33, Yoksam-dong, Kangnam-ku 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	82-2-3458-0700
IV-1-4	Facsimile No.	82-2-553-5254
IV-1-5	e-mail	email@youme.com
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: FR

## PCT REQUEST

Original (for SUBMISSION) - printed on 03.11.2000 09:27:12 AM

V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	CN DE JP US	
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary designations	NONE	
VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	06 July 2000 (06.07.2000)	
VI-1-2	Number	2000-38651	
VI-1-3	Country	KR	
VII-1	International Searching Authority Chosen	Austrian Patent Office (ISA/AT)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	4	-
VIII-2	Description	24	-
VIII-3	Claims	3	-
VIII-4	Abstract	1	abstract.txt
VIII-5	Drawings	0	-
VIII-7	TOTAL	32	
VIII-8	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-9	Fee calculation sheet	✓	-
VIII-9	Separate signed power of attorney	✓	-
VIII-12	Priority document(s)	Item(s) VI-1	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	English	
IX-1	Signature of applicant or agent		
IX-1-1	Name (LAST, First)	KIM, Won-Ho	

## FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	

## PCT REQUEST

OPP000659KR

Original (for SUBMISSION) - printed on 03.11.2000 09:27:12 AM

10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/AT
10-6	Transmittal of search copy delayed until search fee is paid	

## FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>OPP000659KR</b>	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/KR 00/01258</b>	International filing date (day/month/year) <b>3 November 2000 (03.11.2000)</b>	(Earliest) Priority Date (day/month/year) <b>6 July 2000 (06.07.2000)</b>
Applicant <b>LG CHEMICAL LTD. et al.</b>		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (See Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.: \_\_\_\_\_

☐ as suggested by the applicant.

☐ None of the figures.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

## CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: C08L 51/04, C08L 53/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 05 279547 A (Nippon Steel Chem CO) 26 October 1993 (26.10.93) (abstract), Derwent Publications London 1993, Derwent Abstracts AN 1993-374706(47).	1-10
A	JP 6184400 A (Asahi Kasei Kogyo KK) 5 July 1994 (05.07.94) Derwent Publications London 1994, Derwent Abstracts AN 1994-252979(31)	1-10
A	JP 1163209 A (Japan Synthetic Rubber Co Ltd) 27 June 1989 (27.06.89) Derwent Publications London 1989, Derwent Abstract AN 1989-225678	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

„O“ document referring to an oral disclosure, use, exhibition or other means

„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&amp;“ document member of the same patent family

Date of the actual completion of the international search

26 March 2001 (26.03.2001)

Date of mailing of the international search report

11 April 2001 (11.04.2001)

Name and mailing address of the ISA/AT

Austrian Patent Office

Kohlmarkt 8-10; A-1014 Vienna

Facsimile No. 1/53424/535

Authorized officer

TENGLER

Telephone No. 1/53424/213

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/KR 00/01258

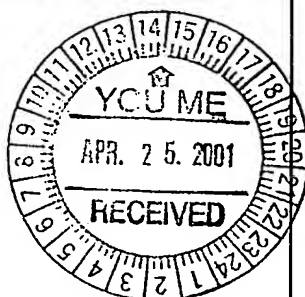
Patent document cited in search report			Publication date	Patent family member(s)		Publication date
JP	A2	5279547	26-10-1993	none		
JP	A2	1163209	27-06-1989	JP	B4 8019199	28-02-1996
JP	A2	6184400	05-07-1994	none		



From the INTERNATIONAL SEARCHING AUTHORITY

To:

KIM, Won Ho  
7th Fl., Teheran Bd., 825-33,  
Yoksam-dong, Kangnam-ku  
Seoul 135-080  
Republic of Korea



## PCT

### NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference <b>OPP000659KR</b>	Date of mailing (day/month/year) <b>11 April 2001 (11.04.01)</b>
International application No. <b>PCT/ KR 00/01258</b>	International filing date (day/month/year) <b>3 November 2000 (03.11.00)</b>
Applicant <b>LG CHEMICAL LTD. et al.</b>	

1. ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

**Filing of amendments and statements under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

**When?** The time limit for filing such amendments is normally two months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.
3. ☐ With regard to the protest against payment of (an) initial fee(s) under Rule 40.2, the applicant is notified that:
- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the text of both the protest decision thereon to the designated Offices
  - ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.
4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis. 1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the IPEA/AT <b>Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200</b>	Authorized officer <p style="text-align: center; font-size: 1.2em;"><b>Wolf</b></p> Telephone No. <b>+43 / 1 / 53424 - 450</b>
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## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article," "Rule" and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended ?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Preliminary Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

**When ?** Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments ?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

**How ?** Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/may accompany the amendments ?

##### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

KIM, Won-Ho  
7th Fl., Teheran Bldg., 825-33  
Yoksam-dong, Kangnam-ke  
Seoul 135-080  
RÉPUBLIQUE DE CORÉE



Date of mailing (day/month/year) 17 September 2001 (17.09.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference OPP000659KR	
International application No. PCT/KR00/01258	
International filing date (day/month/year) 03 November 2000 (03.11.00)	

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

LG CHEMICAL LTD.  
LG Twin Tower  
Yoido-dong 20, Yongdungpo-ku  
Seoul 150-721  
Republic of Korea

State of Nationality

KR

State of Residence

KR

Telephone No.

82-42-866-2072

Facsimile No.

82-42-861-4152

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

LG CHEMICAL CO., LTD.  
LG Twin Tower  
Yoido-dong 20, Yongdungpo-ku  
Seoul 150-721  
Republic of Korea

State of Nationality

KR

State of Residence

KR

Telephone No.

82-42-866-2072

Facsimile No.

82-42-861-4152

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☒ the International Searching Authority ☐ the elected Offices concerned  
☐ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

*E. Carrié*  
Christine Carrié

Telephone No.: (41-22) 338.83.38

## NOTIFICATION OF CHANGE OF

☒ APPLICANT

☐ INVENTOR

To : Commissioner of  
the Korean Industrial Property Office

International Application No.

PCT/KR00/01258

Applicant	Name	LG CHEMICAL, LTD., et al.		Residence Reg. No.		Country of Nationality	Republic of Korea		
	Address	LG Twin Tower, Yoido-dong 20, Yongdungpo-ku, Seoul, Republic of Korea							
Agent	Name	KIM, Won-Ho	Agent's Code	9-1998- 000023-8	Tel. No.	82-2-3458-0700			
	Address	Teheran Bd., 825-33, Yoksam-dong, Kangnam-ku, Seoul, Republic of Korea Fax: +82-2-553-5254 E-mail: <a href="mailto:email@youme.com">email@youme.com</a>							
Cause of Change		Assignment							
Contents of Notification	Former	Name	LG CHEMICAL, LTD.		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	LG Twin Tower, Yoido-dong 20, Yongdungpo-ku, Seoul 150-721, Republic of Korea						
		Name	YOO, Keun-Hoon		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	Hanvit Apt. 123-801, Ahun-dong, Yusung-ku, Taejeon-city, Korea						
		Name	CHOI, Jeong-Su		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	LG Ansan Sataek Sinkwan 307, Ansan-dong, Yosu-city, Chollanam-do, Korea						
		Name	KIM, Sung-Hee		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	LG Ansan Sataek 2 dong 405, Ansan-dong 503-232, Yosu-city, Chollanam-do, Korea						
		Name	LEE, Chan-Hong		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	Lucky Hana Apt. 102-901, Sinsung-dong, Yusung-ku, Taejeon-city, Korea						
	New	Name	LG CHEMICAL CO., LTD.		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	LG Twin Tower, Yoido-dong 20, Youngdungpo-ku, Seoul, 150-721 Republic of Korea						
		Designated State(s)		All Designated States except US					
		Name	YOO, Keun-Hoon		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	Hanvit Apt. 123-801, Ahun-dong, Yusung-ku, Taejeon-city, Korea						
		Designated State(s)		US only					
		Name	CHOI, Jeong-Su		Residence Reg. No.		Country of Nationality	Republic of Korea	
		Address	LG Ansan Sataek Sinkwan 307, Ansan-dong, Yosu-city, Chollanam-do, Korea						
		Designated State(s)		US only					
		Name	KIM, Sung-Hee		Residence Reg. No.		Country of Nationality	Republic of Korea	
Address	LG Ansan Sataek 2 dong 405, Ansan-dong, Yosu-city, Chollanam-do, Republic of Korea								
Designated State(s)		US only							

	Name	LEE, Chan-Hong	Residence Reg. No.		Country of Nationality	Republic of Korea
	Address	Lucky Hana Apt. Taejeon-city, Korea	102-901	Sinsung-dong,	Yusung-ku,	
	Designated State(s)	US only				

Submitted hereby is a notification pursuant to Article 82 of the  
Enforcement Regulations of the Patent Law.

Date(day/month/year) 10 August 2001 (10.08.2001)

Applicant (Agent) KIM, Won-Ho (Seal)



※ Attached Document(s) :

1. A copy of the document(s) substantiating the contents of notification (in case of notification by new applicant)
2. A certified copy of seal impression (in case of notification by new applicant)
3. A copy of the document(s) substantiating the power of attorney, if any

## PCT

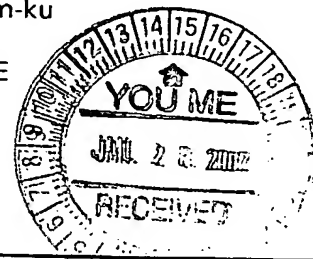
### NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

KIM, Won-Ho  
7th Fl., Teheran Bldg., 825-33  
Yoksam-dong, Kangnam-ku  
Seoul 135-080  
RÉPUBLIQUE DE CORÉE



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**PROCESS FOR PREPARING THERMOPLASTIC TRANSPARENT RESIN****CROSS REFERENCE TO RELATED APPLICATION**

This application is based on application No. 10-2000-0038651 filed  
5 in the Korean Industrial Property Office on July 6, 2000, the content of which  
is incorporated hereinto by reference.

**BACKGROUND OF THE INVENTION****(a) Field of the Invention**

The present invention relates to a process for preparing  
10 thermoplastic transparent resin, more particularly to a process for preparing  
thermoplastic transparent resin having superior moisture, impact and heat  
resistance, natural color, and excellent transparency, which is prepared by  
blending graft transparent resin with methylmethacrylate-styrene-acrylonitrile  
(hereinafter referred to as "MSAN") copolymer after preparing the former  
15 through emulsion polymerization and the latter through bulk polymerization.

**(b) Description of the Related Art**

Recently, studies for providing materials used with high  
functionalities such as transparency, etc. have been strongly and actively  
pursued in order to promote differentiation of product models as industries  
20 advance, and technology continues to change our lives.

For example, studies for newly providing transparency to materials

such as transparent windows of personnel communication systems, covers of washing machines through which machine contents can be seen, monitor housings through which internal components of computer monitors can be seen, game machine housings, transparent windows of home appliances  
5 and office appliances, etc. are intensively being pursued.

However, although acrylonitrile-butadiene-styrene (hereinafter referred to as "ABS") copolymer resin used in these conventional components is superior in terms of qualities such as impact resistance, chemical resistance, processibility, surface glossiness, etc., it is limited in  
10 application to materials in which transparency is required since it is an opaque material because of the nature of the resin.

The conventional technologies for providing plastic materials with transparency include 1) a method using transparent polycarbonate resin; 2) a method for providing transparent polymethyl methacrylate (PMMA) resin  
15 with impact resistance (United States Patent No. 3,787,522 and Japanese Patent Laid-open Publication No. Showa 63-42940); and 3) a method for providing high impact polystyrene (HIPS) resin with transparency (European Patent No. 703,252A2 and Japanese Patent Laid-open Publication No. Heisei 11-147920).

20 However, the method 1) has problems of low chemical resistance and impact resistance at a low temperature, and it is short in processibility thereby limiting application with large scale components, although transparency and impact resistance at ordinary temperature are superior.



The method 2) has an extremely lower impact resistance and a lower chemical resistance thus limiting applications, although transparency and processibility are superior. The method 3) has problems in that chemical resistance and scratch resistance are limited.

5       Therefore, suggested in United States Patent No. 4,767,833 is a process for preparing transparent resin having superior impact resistance, chemical resistance, and processibility by graft copolymerizing styrene-butadiene rubber (SBR) latex with monomers such as methylmethacrylate, styrene, acrylonitrile, etc. in order to solve the problems. However, the  
10 method does not have good impact resistance at a low temperature, and it is limited in obtaining extremely superior transparent resin.

Furthermore, there are problems of deteriorated moisture and heat resistance in which products are discolored into a milky white color by hot water, and problems that products are discolored into a yellowish color by  
15 the influences of residual emulsifiers and coagulants remaining in the final products when the suggested technologies are applied to a product such as a transparent window of a washing machine, which has a great deal of contact with water.

### **SUMMARY OF THE INVENTION**

20       It is an object of the present invention to prepare a thermoplastic resin having excellent impact resistance, chemical resistance, processibility, superior moisture and heat resistance, natural color, etc., and extremely superior transparency by blending graft transparent resin with MSAN

copolymer after preparing graft transparent resin. This is done through emulsion polymerization in a manner whereby a refractive index of conjugated diene rubber latex is similar to that of a mixture of methylmethacrylate, styrene, acrylonitrile, etc. which are grafted to the  
5 conjugated diene rubber latex, and through preparing MSAN copolymer of which a refractive index is similar to that of graft transparent resin through bulk polymerization, in order to solve problems of the conventional technologies.

In order to accomplish the above object, the present invention  
10 provides a process for preparing thermoplastic transparent resin comprising the steps of:

- i ) preparing graft transparent resin by grafting a monomer mixture comprising 20 to 50 parts by weight of conjugated diene rubber latex, 10 to 50 parts by weight of methacrylic acid alkylester  
15 compound or acrylic acid alkylester compound, 5 to 25 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of vinylcyan compound, by emulsion polymerization;
- ii ) preparing methylmethacrylate-styrene-acrylonitrile (MSAN)  
20 copolymer by copolymerizing 50 to 75 parts by weight of methacrylic acid alkylester compound or alkylester compound, 20 to 45 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of vinylcyan compound during bulk polymerization; and

iii) blending the graft transparent resin of step i) with the MSAN copolymer of step ii).

### **DETAILED DESCRIPTION OF THE INVENTION**

In the following detailed description, only the preferred embodiments of the invention have been shown and described, simply by way of illustration of the best mode contemplated by the inventor(s) of carrying out the invention. As will be realized, the invention is capable of modification in various obvious respects, all without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature, and not restrictive.

The present invention is described in detail as follows.

The proper selection of particle diameter and gel content is important since particle diameter, gel content, etc. of conjugated diene rubber latex which is used in preparing graft transparent resin of the present invention greatly influence physical properties such as transparency, impact strength, etc. of a product.

That is, the smaller the particle diameter of the rubber latex, the more superior the transparency is, and the greater the deterioration of the impact strength and fluidity. On the other hand, the larger the particle diameter, the more superior the impact strength is, but the greater the deterioration of the transparency. Furthermore, if gel content of the rubber latex is lower, transparency is deteriorated and impact strength is improved

since many monomers are swelled on the rubber latex during the graft reaction, thereby increasing particle diameter. If the gel content is very high, transparency is superior since less monomers are swelled on the rubber latex, while impact resistance deteriorates since impact absorptivity is  
5 lowered. Therefore, proper selection of gel content is important.

Furthermore, the selection of emulsifiers is important. The selection of emulsifiers which are relatively stable even with pH variation is important since methylmethacrylate monomer causes severe pH variation due to its characteristics thus significantly dropping stability of latex, and its consumed  
10 amount should also be minimized to obtain a transparent resin having superior color, and moisture and heat resistance. Problems have occurred when graft transparent resin has been prepared with the rubber content being low to maintain stability of latex since stability of latex is greatly reduced depending on pH variations, particularly in the preparation process  
15 of graft transparent resin having a high rubber content. Furthermore, in order to prepare transparent resin having superior natural color, moisture and heat resistance, etc. by minimizing emulsifiers and coagulants remaining in the final product, the consumed amount of MSAN copolymer prepared through bulk polymerization should be large in a final product so that the  
20 consumed amount of graft transparent resin prepared by emulsion polymerization can be minimized.

A process for preparing a thermoplastic transparent resin having superior moisture and heat resistance, natural color, etc. in the present

invention can be divided into 1) a preparation process of graft transparent resin, 2) a preparation process of MSAN copolymer, and 3) a preparation process of a transparent resin having superior moisture and heat resistance, natural color, etc. by blending graft transparent resin and MSAN copolymer.

5           1) Preparation process of graft transparent resin

The present invention provides a process for preparing a thermoplastic resin having superior moisture and heat resistance, natural color, impact resistance, etc., and extremely superior transparency after preparing a graft transparent resin having superior impact resistance through  
10 emulsion polymerization by mixing conjugated diene rubber latex having a particle diameter of 2000 to 5000 Å, gel content of 70 to 95%, and a swelling index of 12 to 30 with methacrylic acid alkylester compound, aromatic vinyl compound, vinylcyan compound, etc. so that a refractive index of the mixture can be similar to that of conjugated diene rubber latex,  
15 preparing a copolymer of methacrylic acid ester compound, aromatic vinyl compound, and vinylcyan compound which have similar refractive indexes to that of the graft transparent resin through bulk polymerization, and blending the graft transparent resin with the copolymer.

A refractive index of a monomer mixture used absolutely influences  
20 transparency, and the refractive index is controlled by the consumed amount and mix ratio of the monomer. That is, the consumed amount and mix ratio of the monomer are very important since the refractive index of polybutadiene is about 1.518, thus refractive indexes of all constituents

grafted should be adjusted to a value similar to that in order to have superior transparency. Refractive indexes of each constituents used are 1.49 for methylmethacrylate, 1.59 for styrene, and 1.518 for acrylonitrile.

Furthermore, a thermoplastic transparent resin having superior  
5 transparency can be prepared when a refractive index of MSAN copolymer which is blended with the graft transparent resin is also adjusted to a value which is similar to that of the graft transparent resin. Methods for adding each monomer constituent to rubber latex when preparing graft transparent resin include a method in which each constituent is input in a batch process,  
10 and a method in which the total or partial amount of each monomer constituent is continuously input sequentially. A combined method is used in the present invention in which a batch type and a continuous type of inputting methods are used.

a) Preparation process of rubber latex having small diameter  
15 particles

After putting 100 parts by weight of conjugated diene monomer, 1 to 4 parts by weight of emulsifier, 0.1 to 0.6 parts by weight of polymerization initiator, 0.1 to 1.0 part by weight of electrolyte, 0.1 to 0.5 parts by weight of molecular weight controlling agent, and 90 to 130 parts by weight of ion  
20 exchange water into a reactor in a batch process, the reaction is carried out at a temperature 50 to 65 °C for 7 to 12 hours. And then, conjugated diene rubber latex having small diameter particles with an average particle diameter of 600 to 1500 Å, gel content of 70 to 95%, and swelling index of

about 12 to 30 is prepared by additionally adding a molecular weight controlling agent at 0.05 to 1.2 parts by weight to the reactant, and reacting the resulting mixture at a temperature of 55 to 70 °C for 5 to 15 hours.

Emulsifiers used in the present invention are one or more emulsifiers  
5 selected from the group consisting of alkylaryl sulfonate, alkali methylalkyl sulfate, sulfonated alkylester, soap of fatty acids, alkali salt of abietic acids, and a mixture thereof. A polymerization initiator is water soluble persulfate, peroxy compound, or redox system, and the most preferable water soluble persulfates are sodium and potassium persulfate. Fat soluble  
10 polymerization initiators are one or more initiators selected from the group consisting of cumene hydroperoxide, diisopropylbenzene hydroperoxide, azobisisobutyronitrile, tertiary butyl hydroperoxide, paramethane hydroperoxide, benzoyl peroxide, and a mixture thereof.

Electrolytes are one or more electrolytes selected from the group  
15 consisting of KCl, NaCl,  $\text{KHCO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KHSO}_3$ ,  $\text{NaHSO}_3$ ,  $\text{K}_4\text{P}_2\text{O}_7$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and a mixture thereof. Mercaptan groups are mainly used as the molecular weight controlling agent.

The polymerization temperature is extremely important in adjusting gel content and swelling index of rubber latex, and selection of an initiator  
20 should also be considered at this time.

b) Preparation process of rubber latex having large diameter particles (fusion process of rubber latex having small diameter particles)

Particles were enlarged by agitating the reactant while slowly adding

3.0 to 4.0 parts by weight of acetic acid aqueous solution to 100 parts by weight of rubber latex having small diameter particles of 600 to 1500 Å, gel content of 70 to 95%, and a swelling index of 12 to 30 for 1 hour. After then, rubber latex having large diameter particles of 2000 to 5000 Å, gel content of 70 to 95%, and a swelling index of 12 to 30 was prepared by stopping the agitation. Although a method for obtaining rubber latex which is used to provide for impact resistance can be prepared by a direct polymerization method as disclosed in Japanese Patent Laid-open Publication No. Showa 56-136807, the direct polymerization method takes a lot of reaction time and is limited in obtaining rubber latex having a high gel content. Therefore, preferable is a process in which rubber latex having large diameter particles is prepared by first preparing a high gel content rubber latex having small diameter particles in the above preparation process, and adding acidic materials to the rubber latex so that particles can be enlarged in order to prepare a high gel content rubber latex having large diameter particles within a short time.

#### c) Grafting process

20 to 50 parts by weight of conjugated diene rubber latex prepared in the above process are graft copolymerized using 10 to 50 parts by weight of methacrylic acid alkylester compound or acrylic acid alkylester compound, 5 to 25 parts by weight of aromatic vinyl compound, 1 to 10 parts by weight of vinylcyan compound, 0.2 to 0.6 parts by weight of emulsifier, 0.2 to 0.6 parts by weight of molecular weight controlling agent, 0.05 to 0.3 parts by weight



of polymerization initiator, etc. Emulsifiers used in the polymerization reaction are one or more salts selected from the group consisting of alkylaryl sulfonate, alkali methylalkyl sulfate, sulfonated alkylester, and a mixture thereof. Tertiary dodecyl mercaptan is mainly used as a molecular weight  
5 controlling agent. Redox catalyst which is a mixture of peroxide such as cumene hydroperoxide, diisopropylbenzene hydroperoxide, persulfates, etc., and a reductant such as sodium formaldehyde sulfoxylate, sodium ethylenediamine tetraacetate, primary iron sulfide, dextrose, sodium pyrroline, sodium sulfite, etc. can be used as a polymerization initiator. A  
10 polymerization conversion ratio of latex obtained after terminating the polymerization is 98% or more, and powder is obtained by adding antioxidant and stabilizer to the latex thus coagulating into calcium chloride aqueous solution at a temperature of 80 °C or more, dehydrating, and drying the solution. Whether the above prepared graft copolymer is stable or not is  
15 determined by measuring a solid coagulating fraction (%) as in the following Formula 1:

[Formula 1]

Solid coagulating fraction (%) = (weight of coagulum produced in a reaction vat (g) / total weight of rubber and monomer) X 100

20 When the solid coagulating fraction is 0.7% or more, latex stability is significantly dropped, and it is difficult to obtain graft copolymer which is appropriate to the present invention due to a large amount of coagulum. Mixing ratio of monomer in the present invention is very important in order to

obtain a thermoplastic resin having superior transparency, and of which the refractive index is differentiated according to the mixing ratio. That is, since the refractive index of polybutadiene rubber latex is about 1.518, the total refractive index of a compound which is grafted to the polybutadiene rubber latex should also be similar to that value, and the refractive index of the total compound is preferably in the range of 1.513 to 1.521.

## 2) Preparation process of MSAN copolymers

The preparation process of MSAN copolymers is the bulk polymerization process, wherein the copolymers are prepared by controlling methylmethacrylate monomer, styrene monomer, and acrylonitrile monomer in a proper ratio during the preparation of copolymers through bulk polymerization so that refractive indexes of MSAN copolymers can be similar to the refractive index of graft transparent resin which is blended with these copolymers. 40 to 70 parts by weight of methylmethacrylate, 10 to 30 parts by weight of styrene, and 1 to 10 parts by weight of acrylonitrile as monomers, 26 to 30 parts by weight of toluene as solvent, and ditertiary dodecyl mercaptan as a molecular weight controlling agent are used. The adding amount of the mixed raw material solution is maintained so that average reaction time is 2 hours, and a reaction temperature of 140 to 170 °C is maintained.

The preparation process is a continuous process utilizing a raw material injection pump, a continuous agitating vat, a preheating vat and a volatilizing vat, a polymer transferring pump, and an extruder.

The total refractive index of the copolymer compound should be similar to that of graft transparent resin, and a refractive index of the total compound is preferably in the range of 1.513 to 1.521.

3) Preparation process of transparent resin having superior moisture  
5 and heat resistance, and natural color

After adding MSAN copolymers prepared in the process 2), and filler, antioxidant, and photostabilizer to the graft transparent resin prepared in process 1) and blending them, transparent resin pellets having superior moisture and heat resistance, natural color, etc. are prepared using an  
10 extruding and blending machine at a temperature of 200 to 230 °C. The prepared pellets are again extruded before measuring the physical properties.

The total refractive index of the blended thermoplastic transparent resin is preferably in the range of 1.513 to 1.521.

15 Furthermore, moisture and heat resistance is examined by the deviation between Haze before and after the prepared resin is left at a temperature of 70 °C at 90% humidity for 72 hours. The more Haze deviation ( $\Delta$  Haze), the lower the moisture and heat resistance. Color (value b) is more preferable when it is close to 0 since the closer b is to a  
20 value of 0, the closer to natural color the product is, and the higher the value b is, the more yellowish the product is.

The present invention is described more in detail in the following EXAMPLES, wherein the EXAMPLES are only for exemplifying the present

invention, however the present invention is not limited to the EXAMPLES only.

#### [EXAMPLES]

Evaluation of major physical properties was performed in  
5 EXAMPLES using the following measuring methods:

- a) Izod impact strength was measured according to American Society for Testing and Materials (ASTM) standard D 256;
- b) Haze (transparency) was measured according to ASTM standard D 1003;
- 10 c) b value (color difference: Lab system) was measured according to JIS K-7105; and
- d) Refractive index was measured according to ASTM standard D 542.

#### EXAMPLE 1

15 1) Preparation process of graft transparent resin

a) Preparation process of rubber latex having small diameter particles

After putting 110 parts by weight of ion exchange water, 100 parts by weight of 1,3-butadiene as a monomer, 1.2 parts by weight of the emulsifier  
20 potassium abietate and 1.5 parts by weight of potassium oleate as an emulsifier, 0.1 part by weight of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 0.5 parts by weight of potassium hydrogencarbonate ( $\text{KHCO}_3$ ) as an electrolyte, and 0.3 parts by weight of tertiary dodecyl mercaptan (TDDM) as a molecular weight

controlling agent into a nitrogen substituted polymerization reactor (autoclave) in a batch process and increasing the reaction temperature to 55 °C, the reaction was initiated by adding 0.3 part by weight of potassium persulfate as an initiator to the reactant. After reacting for 10 hours, 0.05  
5 parts by weight of tertiary dodecyl mercaptan was again added to the reactant and reacted at a temperature of 65 °C for 8 hours, thereby terminating the reaction. And then, the obtained rubber latex was analyzed in the following analyzing method.

i ) gel content and swelling index

10 After coagulating the rubber latex using dilute acid or metallic salt, washing, and drying in a dry oven at 60 °C for 24 hours, a lump of rubber was obtained. After cutting the obtained lump of rubber into small pieces, 1 g of rubber fragment was put into 100 g of toluene and stored in a darkroom at room temperature for 48 hours. And then, the rubber fragment was  
15 divided into sol and gel, and gel content and swelling index were measured according to the following Formulae 2 and 3:

[Formula 2]

Gel content (%) = (weight of insoluble gel fragment / weight of sample) X 100

20 [Formula 3]

Swelling index = weight of swelled gel / weight of gel

ii) Particle diameter

Particle diameter was measured with a dynamic laser light scattering

method using 370 HPL of the Nicomp Corporation of the U.S.A. A particle diameter of the obtained rubber latex was about 1000 Å, gel content was 90%, and swelling index was about 18.

b) Preparation process of rubber latex having large diameter  
5 particles (fusion process of rubber latex having small diameter particles)

After putting 100 parts by weight of rubber latex having small diameter particles prepared in the EXAMPLE into a reaction vat, and adjusting reaction speed to 10 rpm and reaction temperature to 30 °C, 3.5 parts by weight of 7% acetic acid aqueous solution were slowly put into the  
10 reactant over 1 hour. Rubber latex having large diameter particles was prepared by leaving the mixture alone for 30 minutes after stopping the agitation. The rubber latex having large diameter particles prepared in the fusion process was analyzed. A particle diameter of the obtained rubber latex was about 3000 Å, gel content of which was 90%, and swelling index  
15 of which was about 17.

c) Grafting process

After putting 40 parts by weight of rubber latex prepared by the above preparation process, 0.1 part by weight of emulsifier alkylaryl sulfonate, 13.68 parts by weight of methylmethacrylate, 5.32 parts by weight  
20 of styrene, 1 part by weight of acrylonitrile, 0.2 parts by weight of tertiary dodecyl mercaptan, 0.048 parts by weight of sodium pyrophosphate, 0.012 parts by weight of dextrose, 0.001 part by weight of primary iron sulfide, and 0.04 parts by weight of cumene hydroperoxide into a nitrogen substituted

polymerization reactor at a temperature of 50 °C in a batch process, the reactant was reacted while increasing the reaction temperature to 73 °C over 1 hour. After continuously putting a mixed emulsifying solution comprising 70 parts by weight of ion exchange water, 0.2 parts by weight of alkylaryl sulfonate, 27.36 parts by weight of methylmethacrylate, 10.64 parts by weight of styrene, 2 parts by weight of acrylonitrile, 0.25 parts by weight of tertiary dodecyl mercaptan, 0.048 parts by weight of sodium pyrophosphate, 0.012 parts by weight of dextrose, 0.001 part by weight of primary iron sulfide, and 0.10 part by weight of cumene hydroperoxide into the reactant for 3 hours and again increasing the reaction temperature to 76 °C, the resultant reactant was aged for 1 hour before terminating the reaction. The polymerization conversion ratio was 99.5%, and the solid coagulated fraction was 0.1%. Thereafter, the latex was coagulated with calcium chloride aqueous solution and washed, thereby obtaining powder.

## 2) Preparation process of MSAN copolymer

A reaction temperature of 157 °C was maintained while continuously putting a raw material in which 68.4 parts by weight of methylmethacrylate, 26.6 parts by weight of styrene, 5 parts by weight of acrylonitrile, 30 parts by weight of solvent toluene, and 0.15 parts by weight of molecular weight controlling agent ditertiary dodecyl mercaptan were mixed into a reaction vat so that average reaction time could be 2 hours. After heating the polymerized solution discharged from a reaction vat at a preheating vat and volatilizing unreacted monomer from a volatilizing vat, a polymer temperature

of 210 °C was maintained so that copolymer resin was processed into a pellet form using a transferring pump and an extruder.

3) Preparation process of transparent resin having superior moisture and heat resistance and natural color.

5        After preparing pellets using a biaxial extruder at a temperature of 210 °C by putting 0.2 parts by weight of filler, 0.1 part by weight of antioxidant, and 0.1 part by weight of photostabilizer into 45 parts by weight of graft transparent resin prepared by the process 1) and 55 parts by weight of MSAN copolymer prepared by the process 2) and blending them, the  
10 pellets were again extruded to prepare transparent resin of which physical properties were measured. Color, moisture and heat resistance, and initial transparency of the resin samples were superior, wherein impact strength was 16, color (value b) was 0.0, initial Haze was 2.3, and Haze deviation after the moisture and heat resistance test was about 5.

15        COMPARATIVE EXAMPLE 1

A transparent resin was prepared in the same method as in the EXAMPLE 1 except that 16 parts by weight of methylmethacrylate, 3 parts by weight of styrene and 1 part by weight of acrylonitrile instead of 13.68 parts by weight of methylmethacrylate, 5.32 parts by weight of styrene, and 1  
20 part by weight of acrylonitrile used in the initial stage of c) grafting process of 1) were used, and 31 parts by weight of methylmethacrylate, 7 parts by weight of styrene, and 2 parts by weight of acrylonitrile instead of 27.36 parts by weight of methylmethacrylate, 10.64 parts by weight of styrene, and 2



parts by weight of acrylonitrile used in the later stage of c) grafting process of 1) were used, and its physical properties were measured. Color, and moisture and heat resistance were superior but initial Haze (transparency) was not good in the transparent resin samples, wherein impact strength was 16.5, color (value b) was 0.15, initial Haze was 9.8, and Haze deviation after the moisture and heat resistance test was about 5. The initial transparency deteriorated due to the refractive index difference between graft transparent resin and MSAN.

#### COMPARATIVE EXAMPLE 2

10 A transparent resin was prepared in the same method as in the EXAMPLE 1 except that 12 parts by weight of methylmethacrylate, 7 parts by weight of styrene and 1 part by weight of acrylonitrile instead of 13.68 parts by weight of methylmethacrylate, 5.32 parts by weight of styrene, and 1 part by weight of acrylonitrile used in the initial stage of c) grafting process of 1) were used, and 25 parts by weight of methylmethacrylate, 13 parts by weight of styrene, and 2 parts by weight of acrylonitrile instead of 27.36 parts by weight of methylmethacrylate, 10.64 parts by weight of styrene, and 2 parts by weight of acrylonitrile used in the later stage of c) grafting process of 1) were used, and its physical properties were measured. Color, and 20 moisture and heat resistance were superior while initial Haze (transparency) was not good in the transparent resin samples, wherein impact strength was 15.5, color (value b) was 0.1, initial Haze was 9.3, and Haze deviation after the moisture and heat resistance test was about 4. The initial transparency

(Haze) deteriorated due to the refractive index difference between graft transparent resin and MSAN.

### COMPARATIVE EXAMPLE 3

A transparent resin was prepared in the same method as in the  
5 EXAMPLE 1 except that 76 parts by weight of methylmethacrylate, 19 parts  
by weight of styrene and 5 parts by weight of acrylonitrile instead of 68.4  
parts by weight of methylmethacrylate, 26.6 parts by weight of styrene, and 5  
parts by weight of acrylonitrile used in the 2) preparation process of MSAN  
copolymer were used, and its physical properties were measured. Color,  
10 and moisture and heat resistance were superior while initial Haze  
(transparency) was not good in the transparent resin samples, wherein  
impact strength was 16, color (value b) was 0.15, initial Haze was 9.4, and  
Haze deviation after the moisture and heat resistance test was about 5.  
The initial transparency (Haze) deteriorated due to the refractive index  
15 difference between graft transparent resin and MSAN.

### COMPARATIVE EXAMPLE 4

A transparent resin was prepared in the same method as in the  
EXAMPLE 1 except that 64 parts by weight of methylmethacrylate, 31 parts  
by weight of styrene and 5 parts by weight of acrylonitrile instead of 68.4  
20 parts by weight of methylmethacrylate, 26.6 parts by weight of styrene, and 5  
parts by weight of acrylonitrile used in the 2) preparation process of MSAN  
copolymer were used, and its physical properties were measured. Color,  
and moisture and heat resistance were superior while initial Haze

(transparency) was not good in the transparent resin samples, wherein impact strength was 15.5, color (value b) was 0.1, initial Haze was 9.9, and Haze deviation after the moisture and heat resistance test was about 5. The initial transparency (Haze) deteriorated due to the refractive index difference between graft transparent resin and MSAN.

#### COMPARATIVE EXAMPLE 5

A transparent resin was prepared in the same method as in the EXAMPLE 1 except that 0.1 part by weight of potassium oleate instead of 0.1 part by weight of emulsifier alkylaryl sulfonate used in the initial stage of c) grafting process of 1) were used. As a result of polymerization, lots of solid coagulum was produced due to the deterioration of latex stability, thereby the result of this method does not fit to the object of the present invention.

#### COMPARATIVE EXAMPLE 6

A transparent resin was prepared in the same method as in the EXAMPLE 1 except that 0.3 parts by weight of potassium oleate instead of 0.1 part by weight of emulsifier alkylaryl sulfonate used in the initial stage of c) grafting process of 1) were used, and its physical properties were measured. Color was not good, and moisture and heat resistance were also sub-standard in the transparent resin samples, wherein impact strength was 16, color (value b) was 2.8, initial Haze was 4.5, and Haze deviation after the moisture and heat resistance test was about 17.

#### COMPARATIVE EXAMPLE 7

A transparent resin was prepared in the same method as in the EXAMPLE 1 except the following.

After putting 18 parts by weight of rubber latex, 90 parts by weight of ion exchange water, 0.1 part by weight of emulsifier alkylaryl sulfonate, 13.68 parts by weight of methylmethacrylate, 5.32 parts by weight of styrene, 1 part by weight of acrylonitrile, 0.2 parts by weight of tertiary dodecyl mercaptan, 0.048 parts by weight of sodium pyrophosphate, 0.012 parts by weight of dextrose, 0.001 part by weight of primary iron sulfide, and 0.04 parts by weight of cumene hydroperoxide into a reactor at a temperature of 50 °C in a batch process, the reaction was performed while increasing the reaction temperature to 73 °C over 1 hour. After continuously adding a mixed emulsifying solution comprising 70 parts by weight of ion exchange water, 0.2 parts by weight of alkylaryl sulfonate, 43.2 parts by weight of methylmethacrylate, 16.8 parts by weight of styrene, 2 parts by weight of acrylonitrile, 0.25 parts by weight of tertiary dodecyl mercaptan, 0.048 parts by weight of sodium pyrophosphate, 0.012 parts by weight of dextrose, 0.001 part by weight of primary iron sulfide, and 0.10 part by weight of cumene hydroperoxide into the reactant over 3 hours and again increasing the reaction temperature to 76 °C, the resulting reactant was aged for 1 hour, thereby terminating the reaction. The polymerization conversion ratio was 99.8%, and the solid coagulated fraction was 0.05%. Thereafter, the latex was coagulated with calcium chloride aqueous solution and washed, thereby obtaining powder.

Furthermore, after preparing pellets using a biaxial extruder at a temperature of 210 °C by putting 0.2 parts by weight of filler, 0.1 part by weight of antioxidant, and 0.1 part by weight of photostabilizer into 100 parts by weight of powder obtained in the 1) preparation process of graft  
5 transparent resin without a preparation process of MSAN copolymer and blending them, the pellets were again extruded to prepare transparent resin of which physical properties were measured. Color was not good, and moisture and heat resistance, etc. were also deteriorated in the transparent resin samples, wherein impact strength was 16.5, color (value b) was 3.2,  
10 initial Haze was 4.9, Haze deviation after the moisture and heat resistance test was about 12.

A preparation process of thermoplastic transparent resin according to the present invention can prepare a thermoplastic transparent resin having excellent impact resistance, chemical resistance, processibility, etc., superior  
15 moisture and heat resistance, natural color, etc., and extremely superior transparency after preparing a graft transparent resin having superior impact resistance, transparency, etc. through emulsion polymerization by employing methylmethacrylate and controlling contents and mixing ratios of each constituent employed so that the refractive index of conjugated diene rubber  
20 latex can be similar to that of a mixture of methylmethacrylate, styrene, acrylonitrile, etc. which are grafted to the conjugated diene rubber latex in preparing acrylonitrile-butadiene-styrene (ABS) resin comprising acrylonitrile providing superior chemical resistance, butadiene providing superior impact

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resistance, and styrene providing superior processibility, preparing an MSAN copolymer of which the refractive index is similar to that of graft transparent resin in the emulsion polymerization process, and blending the graft transparent resin with the MSAN copolymer.

5           While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

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**WHAT IS CLAIMED IS:**

1. A process for preparing thermoplastic transparent resin comprising

the steps of:

- 5           i ) preparing graft transparent resin by grafting a monomer mixture comprising 20 to 50 parts by weight of conjugated diene rubber latex, 10 to 50 parts by weight of methacrylic acid alkylester compound or acrylic acid alkylester compound, 5 to 25 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of vinylcyan compound  
10           through emulsion polymerization;
- ii ) preparing methylmethacrylate-styrene-acrylonitrile (MSAN) copolymer by copolymerizing 50 to 75 parts by weight of methacrylic acid alkylester compound or alkylester compound, 20 to 45 parts by weight of aromatic vinyl compound, and 1 to 10 parts by weight of  
15           vinylcyan compound during bulk polymerization; and
- iii) blending the graft transparent resin of step i ) with the MSAN copolymer of step ii).

2. The process for preparing thermoplastic transparent resin according to claim 1, wherein a difference of refractive index between the  
20   conjugated diene rubber latex and monomer mixture grafted is within the range of 0.004.

3. The process for preparing thermoplastic transparent resin according to claim 1, wherein a difference of refractive index between the

conjugated diene rubber latex and MSAN copolymer is within the range of 0.004.

4. The process for preparing thermoplastic transparent resin according to claim 1, wherein the conjugated diene rubber latex is an  
5 aliphatic conjugated diene compound, or a mixture of an aliphatic conjugated diene compound and an ethylene based unsaturated monomer.

5. The process for preparing thermoplastic transparent resin according to claim 1, wherein the conjugated diene rubber latex has an average particle diameter of 2000 to 5000 Å, a gel content of 70 to 95%,  
10 and a swelling index of 12 to 30.

6. The process for preparing thermoplastic transparent resin according to claim 1, wherein the methacrylic acid alkylester compound or acrylic acid alkylester compound is methylmethacrylate.

7. The process for preparing thermoplastic transparent resin  
15 according to claim 1, wherein the aromatic vinyl compound is a compound selected from the group consisting of styrene, *a* -methylstyrene, *o* -ethylstyrene, *p* -ethylstyrene, and vinyltoluene.

8. The process for preparing thermoplastic transparent resin according to claim 1, wherein the vinylcyan compound is a compound  
20 selected from the group consisting of acrylonitrile, methacrylonitrile, and ethacrylonitrile.

9. The process for preparing thermoplastic transparent resin according to claim 1, wherein the emulsion polymerization of step i) is



carried out using a mixture of one or more emulsifiers selected from the group consisting of alkylaryl sulfonate salts, alkali methylalkyl sulfate salts, and sulfonated alkylester salts.

10. The process for preparing thermoplastic transparent resin  
5 according to claim 1, wherein the emulsion polymerization of step i ) and bulk polymerization of step ii) are carried out using one or more polymerization initiators selected from the group consisting of cumene hydroperoxide, diisopropylbenzene hydroperoxide, and persulfate.

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